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Thermochemical Studies on Rare Earth Diglycolate Complexes.

- I. Stability Constants and Free Energy Changes at 5, 20, 35, and 50 °C.

Heikki Ots

Division of Physical Chemistry, Chemical Center, University of Lund,
P.O.B. 740, S-220 07 Lund 7, Sweden.

The stability constants for the diglycolato complexes of four tervalent rare earths have been determined at 5, 20, 35, and 50 °C. The rare earths selected for the investigation were Pr(III), Sm(III), Dy(III) and Yb(III). The stability constants were obtained by a potentiometric standard method and all data refer to an aqueous sodium perchlorate medium with the total sodium ion concentration equal to 1.00 M. The changes in free energy were calculated from the stability constants and the temperature dependence was then compared with the results obtained from a calorimetric investigation.



An investigation of the changes in free energy, enthalpy and entropy for the formation of rare earth diglycolato complexes in an aqueous perchlorate medium has previously been made at this laboratory^{1,2}. This and similar studies³⁻⁹ have established that there is no simple relationship between the changes in the thermodynamic quantities and the ionic radius of the rare earth ions. From the fact that the variations in ΔG° , ΔH° and ΔS° through the lanthanoid series were approximately the same for most of the ligands studied, it could be concluded that a large part of the variation could be ascribed to some property of the central ion. There is some evidence^{4,10} that this property is the state of hydration of the central ion¹². Owing to the lanthanoid contraction a change in hydration number may occur somewhere in the middle of the series.

It is difficult to give a microscopic interpretation of macroscopic thermodynamic data in a system of strongly interacting particles. It must be realized that no quantitative molecular interpretation of the thermodynamics of complex formation reactions is possible until a quantitative theory for concentrated electrolyte solutions is available. Until then all molecular interpretations are necessary qualitative and are obtained mainly by correlations between thermodynamic and non-thermodynamic data e.g. kinetic¹¹ or spectroscopic¹³.

Another difficulty when trying to interpret changes in thermodynamic quantities is to decide whether the change is caused mainly by one or by several of the species participating in the reaction. The difficulty can in some cases be avoided by systematic variations of metal ion and ligand; a method used previously in this series of



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investigations. Interpretations of thermodynamic data for formation of complexes would be facilitated if the partial molar contribution from each species to the observed change of state could be determined.

In order to gather information of this kind we have investigated how the enthalpy changes for the formation of some rare earth diglycolate complexes vary with temperature. The changes in heat capacity, $\Delta C_{p,j}^{\circ}$, thus obtained in combination with the partial molal heat capacities for the various rare earth perchlorates, makes it possible to determine the variation of the partial molal heat capacities for the various complexes through the lanthanide series. This is thus a way to get a more detailed information about the thermodynamics of complex formation than that obtained from free energy and enthalpy measurements alone.

In a previous publication¹⁴ we have reported the construction of a titration calorimeter capable of giving enthalpy data accurate enough to permit reliable calculations of the heat capacity changes for the reactions studied. By means of this calorimeter the temperature dependences of the reaction enthalpies were determined for nine lanthanoid diglycolato systems in the temperature range 5-50 °C¹⁵

In the present work, four model systems have been chosen for a study of the rare earth diglycolate complex formation reactions as a function of temperature. These systems have been fully investigated, i.e. both the changes in free energy and enthalpy have been determined. For other systems, only the enthalpy changes have been measured while the stability constants and the free energy changes have been calculated on the basis of these measurements¹⁵ and the known stability constants at 20 °C.

The central ions in the four model systems were Pr(III), Sm(III), Dy(III) and Yb(III). The stability constants were determined at 5, 20, 35, and 50 °C. The measurements were made by a potentiometric standard method¹ and the stability constants were computed by a least-squares program developed by Sillén and Ingri¹⁶. The constants

refer to an aqueous sodium perchlorate medium with 1.00 M total sodium ion concentration. All concentrations given in this paper are in $\text{mol}\cdot\text{l}^{-1}$ at 25 °C. The notations used are the same as before^{1,2}.

In order to check the results from the computer, the stability constants were also determined graphically by means of the integral:

$$\ln \frac{\bar{X}[A]_j}{\bar{X}[A]_i} = \int_{[A]_i}^{[A]_j} \frac{\bar{n}}{[A]} d[A] \quad (1)$$

For further details see Ref¹ and Ref¹⁷.

The stability constants for the diglycolic acid were calculated by the method of Leden and Fronæus¹⁸.

EXPERIMENTAL

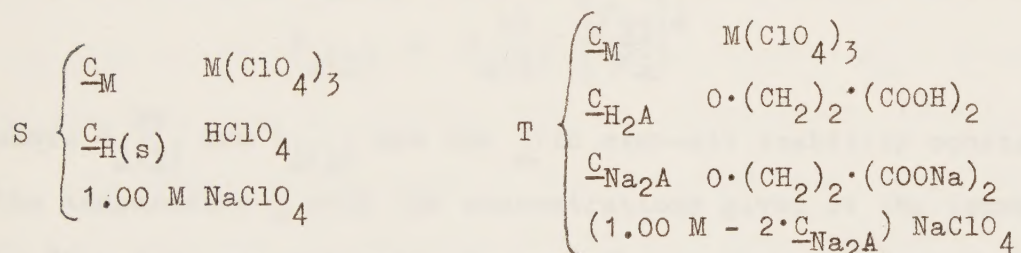
Chemicals. The various rare earth oxides were obtained from the Potash & Chemical Corporation. Stock solutions of the rare earth perchlorates were prepared and analyzed as described before¹⁹. The diglycolic acid was obtained from Fluka A. G. and was recrystallized from ethyl acetate. The equivalent weight of the acid was determined to 67.0 ± 0.1 (calc. 67.0). The diglycolate buffers used in the potentiometric titrations were prepared by partial neutralization of the acid with sodium hydroxide. The sodium perchlorate was prepared from perchloric acid (Baker's analyzed) and sodium carbonate (Merck p.a.) according to a method described earlier²⁰.

Potentiometric titrations: The stability constants for the systems investigated were determined by measuring the emf of galvanic cells of the following composition:

Au	$\frac{C_M}{C_{H_2A}}$	$M(ClO_4)_3$			
	$O \cdot (CH_2)_2 \cdot (COOH)_2$				
	$\frac{C_{Na_2A}}{C_{Na_2A}}$	$O \cdot (CH_2)_2 \cdot (COONa)_2$		0.025 M NaCl	
	$(1.00 \text{ M} - \frac{v \cdot 2C_{Na_2A}}{V_o + v}) ClO_4^-$		1.00 M NaClO ₄	0.975 NaClO ₄	Ag, AgCl
	1.00 M Na ⁺				
	Quinhydrone				

The temperature of the right half-cell was kept constant at 25.00 °C. The titrations were performed in the left half-cell at 5.00, 20.00, 35.00, and 50.00 °C. In order to obtain better thermal stability and to avoid condensation on the walls at the higher temperatures, a special titration vessel with a thermostated top lid was used.

The solutions in the left half-cell were prepared by adding small amounts ($\underline{v}$ ml) of a solution T to a known volume (25.00 ml = $\underline{V_o}$) of a solution S. The additions were made by calibrated piston burettes at 25 °C. The solutions S and T had the following compositions:



The sodium ion concentration was equal to 1.00 M in all the measurements i.e. the perchlorate concentration varied slightly through the titration. This change did not influence the experimental results as indicated by the fact that measurements performed with a constant sodium perchlorate concentration equal to 1.00 M gave an experimental $\bar{n}$ -curve coinciding with the one obtained from

measurements where the sodium ion concentration was kept constant. This check was made only for the samarium system at 20 °C.

The measurements have been carried out at two different buffer compositions. In each series the values of $\underline{C}_A$ and $\underline{C}_M$ were kept constant. The measured electromotoric farces, $\underline{E}$, of the ^{cells} used have been corrected for the liquid junction potentials. The corrections have been made according to a method described by Ahrlund²¹, assuming that the junction potential depends only on the hydrogen ion concentration.

The reliability of the quinhydrone electrode was checked against the glass electrode at 5 and 50 °C. The difference between the two electrodes never exceeded 0.2 mV.

At all temperatures the additions, volumes and concentrations refer to 25 °C. The constants, $\beta_{j(\underline{t})}^{25}$, calculated from this type of data are related to the true stability constants, $\beta_{j(\underline{t})}$, on the molar scale according to the equation:

$$\beta_{j(\underline{t})} = \beta_{j(\underline{t})}^{25} \cdot \left[\frac{\rho_{25}}{\rho_{\underline{t}}} \right]^j \quad (2)$$

where $\beta_{j(\underline{t})}^{25}$ and $\beta_{j(\underline{t})}$ are the j:th over-all stability constants at the temperature t with the concentrations given at the temperatures 25 °C and t, respectively. ρ_{25} and $\rho_{\underline{t}}$ are the densities of the solution at the corresponding temperatures.

If the solution can be regarded as dilute, the weight of the solute can be neglected and the densities of the solution can be replaced by the densities of the solvent. From equation (2) we then get:

$$\beta_{j(\underline{t})} \cdot \rho_{\underline{t}}^j = \beta_{j(\underline{t})}^{25} \cdot \rho_{25}^j = \beta_{j(\underline{t})}^{(\underline{m})} \quad (3)$$

where $\beta_{j(t)}^{(m)}$ is given on the molality scale. Under these conditions the relationship between the stability constants given on different concentration scales and the reaction enthalpies can be described according to the equations:

$$\frac{\delta \ln \beta_{j(c)}}{\delta T} = \frac{\Delta H_j^0}{RT^2} - j \frac{\delta \ln \rho}{\delta T} \quad (4)$$

$$\frac{\delta \ln \beta_{j(m)}}{\delta T} = \frac{\Delta H_j^0}{RT^2} \quad (5)$$

where $\beta_{j(c)}$ and $\beta_{j(m)}$ are the over-all stability constants expressed on the molar and molal scale, respectively and ρ is the density of the solvent. It is thus convenient in the calculations to use either $\beta_{j(m)}$ or $\beta_{j(c)}$, provided that the density derivate is zero.

In this investigation we have consistently expressed all stability constants as $\beta_{j(t)}^{25}$ i.e. quantities proportional to the corresponding constants on the molality scale. These stability constants can thus directly be used in eqn. (5) to compute ΔH_j^0 , which may then be compared with the results from the calorimetric investigations.

To permit calculations of the true stability constants, $\beta_{j(t)}$, we have measured the density at different temperatures of a 1.05 mol.kg⁻¹ (1.00 M at 25 °C) sodium perchlorate solution which may be regarded as the solvent in this particular case. The following densities were obtained:

$t/^\circ\text{C}$	$\rho/\text{g}\cdot\text{cm}^{-3}$
5	1.08281
20	1.07739
25	1.07556
35	1.07074
50	1.05888

The correction is largest for β_3 at 5 °C and 50 °C where it amounts to about 5 %.

R E S U L T S

The proton diglycolate system.

The formation constants, $\delta_{\pm}$, of the diglycolate acid were determined at 5, 20, 35, 50, and 65 °C. The measurements were made at $C_M = 0$ in the same type of galvanic cells as described before. Two different total concentrations of ligand were used ($C_A = 25$ mM and $C_A = 50$ mM). The corrections for the liquid junction potential did not exceed 0.4 mV.

The experimental data are given in Tables 1-5. The formation constants with their estimated errors are given in Table 6 and the stepwise free energy changes with their corresponding errors (see below) are shown in Table 7.

The rare earth diglycolate systems.

All the measurements have been made with two different T-solutions with the buffer ratios C_{H_2A}/C_{Na_2A} equal to 0.52 and 1.00, respectively. The corrections for the liquid junction potential were all in the range from 0 to 1.1 mV.

The experimental results for the four lanthanoid diglycolato systems investigated are collected in Tables 8-23. The stability constants with their corresponding errors are given in Table 24. The errors given in the over-all constants are equal to three standard deviations.

The deviations in the stepwise stability constants have been calculated by addition of relative errors e.g.

$$\frac{\Delta K_2}{K_2} = \frac{\Delta \beta_2}{\beta_2} + \frac{\Delta \beta_1}{\beta_1}$$

The stepwise free energy changes with their corresponding errors are shown in Table 25.

The experimental data for the praseodymium diglycolate system are also given in Figure 1 as plots of $\bar{n}$ versus $\log[A]$ at four temperatures. The fulldrawn curves were computed from the constants in Table 24. The plots show that the stability constants used are in good agreement with the experimental data. This conclusion is also true for the other systems investigated.

Discussion

Several investigations have been published, where enthalpy changes and, in some cases, even heat capacity changes have been computed from the temperature dependence of the corresponding free energy changes. The ΔH° and ΔC_p° data obtained in this way are usually fairly uncertain due to propagation of errors when first and second temperature derivatives are calculated from experimental free energy data determined at various temperatures. It is generally agreed that direct calorimetric measurements give the most accurate values of ΔH° and ΔC_p° . It is possible to make a direct comparison of the two methods by using the data in this and the following communication¹⁵.

In Figure 2, the stepwise free energy changes, $\frac{\Delta G_1^\circ}{T}$ and $\frac{\Delta G_2^\circ}{T}$, for the protonation of diglycolate, have been plotted as functions of temperature. The fulldrawn curves are calculated from $\Delta H_j^\circ(T)$ -data¹⁵ using best fit to the corresponding free energy data. The agreement between the two sets of measurements is satisfactory as seen from the differences between the observed and calculated protonation constants given in the tables of Figure 2. The differences are also in accordance with the estimated errors in the potentiometric values. It can be concluded that no systematic errors have been introduced in

the determinations of $\underline{\Delta G}_1^{\circ}$ as a function of temperature. The calculated constants have been obtained from the free energy functions given in Table 26.

An error in the protonation constants affects the values of the corresponding enthalpy and heat capacity changes. By using expressions derived by King²³ and Please²⁴ and the estimated errors of the stepwise constants, it is found that the uncertainties in $\underline{\Delta H}_1^{\circ}$ and $\underline{\Delta H}_2^{\circ}$ at 25 °C are $\pm 120 \text{ cal}\cdot\text{mol}^{-1}$ and $\pm 250 \text{ cal}\cdot\text{mol}^{-1}$, respectively. These values corresponds to errors of $\pm 15 \%$ and $\pm 100 \%$ in the known enthalpy changes. In spite of the rather accurate determinations of $\underline{K}_1$ it is thus impossible to get more than a very rough estimate of the corresponding enthalpy change. Values of the heat capacity change can obviously not be obtained at all from the free energy data.

The corresponding values of $\underline{\Delta G}_1^{\circ}/\underline{T}$, $\underline{\Delta G}_2^{\circ}/\underline{T}$ and $\underline{\Delta G}_3^{\circ}/\underline{T}$ vs $\underline{T}$ for the samarium diglycolate system are shown in Figures 3 and 4. The full drawn curves have been obtained from enthalpy data as described before. The equations for the curves are given in Table 26.

It is obvious from these graphs that the differences between the observed and calculated stability constants are much larger for the samarium diglycolate than for the proton diglycolate system. The $\underline{\Delta G}_2^{\circ}/\underline{T}$ and $\underline{\Delta G}_3^{\circ}/\underline{T}$ plots in Figures 3 and 4 show, however, that these differences are in most instances within the error limits given.

An exception is the $\underline{\Delta G}_1^{\circ}/\underline{T}$ plot where the error limits given are too low. More realistic errors are obtained if the deviations in $\underline{\beta}_1$ (Table 24) are multiplied by a factor two.

We do not think that this is a result of a systematic error in the titration procedure, c.f. the protonation constant data. It is more probable, in our opinion, that the standard deviations in the least-squares refinement of the stability constants do not always represent realistic error estimates. It is well known that the standard deviations are strongly dependent on the weighting scheme used. Our choice of giving a unit weight to all experimental quantities might thus not be the best one.

This weighting scheme must especially be questioned for low values of $\bar{n}$. Because of the very unfavourable ratios between β_1 and the protonation constants δ_1 and δ_2/δ_1 , it is not possible to determine $[A]$ accurately for low values of $\bar{n}$. This has in our case partly been circumvented by choice of the lower integration limit in a region where accurate $\bar{n}$ - $[A]$ values can be determined. The choice is, however, subjective and a different weighting scheme for the lower $\bar{n}$ -values would perhaps have given more realistic errors in β_1 .

On the basis of the large errors in the stepwise constants there would be no sense in calculating the enthalpy changes from the corresponding free energy data.

The three other rare earth diglycolate systems investigated show the same behaviour as the samarium system.

The stability constants at 20 °C obtained in this study are slightly different from those obtained earlier¹. The reason for this is to be found in an erroneous correction for the liquid junction potential in the earlier work. This error is only made in the determinations of the δ_j -values. A recalculation of the data from the praseodymium diglycolate system in the previous investigation using the correct δ_j -values gives an $\bar{n}$ -curve which almost coincides with

the one obtained in the present investigation.

A discussion of the observed dependence of the various thermodynamic functions on temperature will be given in the following communication¹⁵.

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Table 1. Corresponding values of v , $-\log[H]$ and $\bar{n}_H$ for the propanedioic acid-diglycolate system at 5.00 °C.

S: $C_A=0.0504$ M, $C_H=0.0006$ M, $C_{Na}=1.00$ M S: $C_A=0.0252$ M, $C_H=0.0003$ M, $C_{Na}=1.00$ M
I: $C_A=0.0498$ M, $C_H=0.0997$ M, $C_{Na}=1.00$ M T: $C_A=0.0249$ M, $C_H=0.0498$ M, $C_{Na}=1.00$ M
 $V_0=25.00$ ml $V_0=25.00$ ml

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	5.6837	0.0119
1.00	4.7600	0.0872
2.49	4.3853	0.1893
2.98	4.3054	0.2206
4.97	4.0753	0.3368
7.46	3.8888	0.4623
9.95	3.7475	0.5698
12.93	3.6189	0.6798
17.90	3.4577	0.8290
24.87	3.2911	0.9876
31.84	3.1643	1.1063
39.80	3.0538	1.2100

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	5.6920	0.0119
1.00	4.7671	0.0872
2.49	4.3923	0.1893
3.48	4.2150	0.2500
4.97	4.0826	0.3368
6.96	3.9268	0.4750
9.95	3.7540	0.5698
12.44	3.6461	0.6500
20.90	3.3871	0.8290
25.87	3.2807	0.9250
39.80	3.0737	1.1063

G: $C_A=0.0498$ M, $C_H=0.0997$ M, $C_{Na}=1.00$ M S: $C_A=0.0249$ M, $C_H=0.0498$ M, $C_{Na}=1.00$ M
I: $C_A=0.0504$ M, $C_H=0.0006$ M, $C_{Na}=1.00$ M T: $C_A=0.0259$ M, $C_H=0.0003$ M, $C_{Na}=1.00$ M
 $V_0=25.00$ ml $V_0=25.00$ ml

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	2.0866	1.8356
1.49	2.2532	1.7751
2.98	2.3963	1.7057
4.97	2.5539	1.6114
7.46	2.7115	1.5002
9.95	2.8346	1.4002
17.90	3.1136	1.1498

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	2.2550	1.7767
1.49	2.3764	1.7180
2.98	2.4869	1.6554
4.97	2.6209	1.5710
7.46	2.7567	1.4800
9.95	2.8709	1.3750
12.93	2.9850	1.2750
29.85	3.3871	0.8949

Table 2. Corresponding values of $\underline{v}$, $-\log[H]$ and $\bar{n}_H$ for the proton diglycolate system at 20.00 °C.

S: $C_A=0.0504$ M, $C_H=0.0006$ M, $C_{Na}=1.00$ M S: $C_A=0.0252$ M, $C_H=0.0003$ M, $C_{Na}=1.00$ M
T: $C_A=0.0498$ M, $C_H=0.0997$ M, $C_{Na}=1.00$ M T: $C_A=0.0249$ M, $C_H=0.0498$ M, $C_{Na}=1.00$ M
 $V_O=25.00$ ml $V_O=25.00$ ml

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	5.7415	0.0119
1.00	4.7969	0.0872
2.49	4.4131	0.1894
2.98	4.3306	0.2206
4.97	4.1004	0.3369
7.46	3.9079	0.4624
9.95	3.7687	0.5700
12.93	3.6381	0.6800
17.90	3.4697	0.8292
31.84	3.1724	1.1066
39.80	3.0607	1.2102

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	5.7398	0.0119
1.00	4.7929	0.0868
2.49	4.4114	0.1885
3.48	4.2636	0.2502
4.97	4.0986	0.3351
6.96	3.9423	0.4364
9.95	3.7704	0.5664
12.44	3.6604	0.6585
16.42	3.5161	0.7822
20.90	3.3941	0.8953
25.87	3.2875	0.9963
31.84	3.1844	1.0937
39.80	3.0761	1.1936

S: $C_A=0.0498$ M, $C_H=0.0997$ M, $C_{Na}=1.00$ M S: $C_A=0.0249$ M, $C_H=0.0498$ M, $C_{Na}=1.00$ M
T: $C_A=0.0504$ M, $C_H=0.0006$ M, $C_{Na}=1.00$ M T: $C_A=0.0259$ M, $C_H=0.0003$ M, $C_{Na}=1.00$ M
 $V_O=25.00$ ml $V_O=25.00$ ml

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	2.0914	1.8375
1.49	2.2547	1.7755
2.98	2.4008	1.7065
4.97	2.5589	1.6120
7.46	2.7170	1.5007
9.95	2.8407	1.4006
12.93	2.9679	1.2948
17.90	3.1294	1.1503
24.87	3.2978	0.9929

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	2.2547	1.7766
1.49	2.3784	1.7188
2.98	2.4936	1.6574
7.46	2.7599	1.4692
9.95	2.8751	1.3755
12.93	2.9919	1.2763
16.91	3.1174	1.1529

Table 3. Corresponding values of $\underline{v}$, $-\log[H]$ and $\bar{n}_H$ for the proton diglycolate system at 35.00 °C.

S: $C_A=0.0504$ M, $C_H=0.0006$ M, $C_{Na}=1.00$ M S: $C_A=0.0252$ M, $C_H=0.0003$ M, $C_{Na}=1.00$ M
T: $C_A=0.0498$ M, $C_H=0.0997$ M, $C_{Na}=1.00$ M T: $C_A=0.0249$ M, $C_H=0.0498$ M, $C_{Na}=1.00$ M
 $V_O=25.00$ ml $V_O=25.00$ ml

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
2.49	4.4179	0.1956
2.98	4.3411	0.2269
4.97	4.1154	0.3435
7.46	3.9241	0.4691
9.95	3.7819	0.5766
12.93	3.6478	0.6867
17.90	3.4778	0.8357
24.87	3.3044	0.9938
31.84	3.1720	1.1123
39.80	3.0576	1.2153

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	5.4693	0.0179
1.00	4.7760	0.0932
2.49	4.4196	0.1954
3.48	4.2740	0.2573
4.97	4.1187	0.3426
7.46	3.9241	0.4676
9.95	3.7819	0.5743
12.93	3.6494	0.6833
17.90	3.4827	0.8302
25.37	3.2979	0.9945

S: $C_A=0.0498$ M, $C_H=0.0997$ M, $C_{Na}=1.00$ M S: $C_A=0.0249$ M, $C_H=0.0498$ M, $C_{Na}=1.00$ M
T: $C_A=0.0504$ M, $C_H=0.0006$ M, $C_{Na}=1.00$ M T: $C_A=0.0259$ M, $C_H=0.0003$ M, $C_{Na}=1.00$ M
 $V_O=25.00$ ml $V_O=25.00$ ml

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$
0	2.0749	1.8317
1.49	2.2417	1.7736
2.98	2.3888	1.7062
4.97	2.5474	1.6133
7.46	2.7060	1.5033
9.95	2.8352	1.4045
12.93	2.9611	1.3001
17.90	3.1246	1.1554
24.87	3.2963	0.9988

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	2.2433	1.7722
1.49	2.3659	1.7168
2.98	2.4787	1.6557
4.97	2.6079	1.5723
7.46	2.7469	1.4719
9.95	2.8613	1.3798
12.93	2.9807	1.2811
17.90	3.1393	1.1427
24.87	3.3044	0.9902

Table 4. Corresponding values of y , $-\log[H]$ and $\bar{n}_H$ for the proton diglycolate system at 50.00 °C.

S: $C_A=0.0504$ M, $C_H=0.0006$ M, $C_{Na}=1.00$ M S: $C_A=0.0252$ M, $C_H=0.0003$ M, $C_{Na}=1.00$ M
T: $C_A=0.0498$ M, $C_H=0.0997$ M, $C_{Na}=1.00$ M T: $C_A=0.0249$ M, $C_H=0.0498$ M, $C_{Na}=1.00$ M
 $V_O=25.00$ ml $V_O=25.00$ ml

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	5.5301	0.0187
1.00	4.8238	0.0943
2.49	4.4637	0.1967
2.98	4.3857	0.2280
4.97	4.1565	0.3445
7.46	3.9648	0.4701
9.95	3.8229	0.5777
12.93	3.6857	0.6878
17.90	3.5126	0.8368
31.84	3.1977	1.1135

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	5.5504	0.0186
1.00	4.8223	0.0941
2.49	4.4621	0.1964
3.48	4.3140	0.2583
4.97	4.1550	0.3436
6.96	3.9959	0.4452
9.45	3.8447	0.5552
12.44	3.7028	0.6679
16.42	3.5578	0.7916
20.90	3.4284	0.9046
25.87	3.3131	1.0054
31.84	3.2084	1.1018
39.80	3.0886	1.2017

S: $C_A=0.0498$ M, $C_H=0.0997$ M, $C_{Na}=1.00$ M S: $C_A=0.0249$ M, $C_H=0.0498$ M, $C_{Na}=1.00$ M
T: $C_A=0.0504$ M, $C_H=0.0006$ M, $C_{Na}=1.00$ M T: $C_A=0.0259$ M, $C_H=0.0003$ M, $C_{Na}=1.00$ M
 $V_O=25.00$ ml $V_O=25.00$ ml

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	2.0814	1.8343
1.49	2.2466	1.7749
2.98	2.3901	1.7066
4.97	2.5491	1.6082
7.46	2.7128	1.5042
9.95	2.8438	1.4054
12.93	2.9716	1.3010
17.90	3.1400	1.1564
24.87	3.3177	0.9998

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
4.97	2.6115	1.5733
7.46	2.7518	1.4729
9.95	2.8718	1.3813
12.93	2.9903	1.2823
16.91	3.1229	1.1692
22.88	3.2819	1.0308

Table 5. Corresponding values of $\underline{v}$, $-\log[H]$ and $\bar{n}_H$ for the proton diglycolate system at 65.00 °C.

S: $C_A=0.0504$ M, $C_H=0.0006$ M, $C_{Na}=1.00$ M S: $C_A=0.0252$ M, $C_H=0.0003$ M, $C_{Na}=1.00$ M
T: $C_A=0.0498$ M, $C_H=0.0997$ M, $C_{Na}=1.00$ M T: $C_A=0.0249$ M, $C_H=0.0498$ M, $C_{Na}=1.00$ M
 $V_o=25.00$ ml $V_o=25.00$ ml

V_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	5,5840	0,0187
1,00	4,8838	0,0943
2,49	4,5265	0,1968
2,98	4,4487	0,2281
4,97	4,2193	0,3447
7,46	4,0241	0,4704

V_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	5,5840	0,0186
1,00	4,8823	0,0942
2,49	4,5218	0,1965
3,48	4,3757	0,2585
4,97	4,2133	0,3440
6,96	4,0524	0,4457
9,45	3,9005	0,5559
12,44	3,7589	0,6688
16,42	3,6100	0,7928
20,90	3,4774	0,9062
25,87	3,3611	1,0074
31,84	3,2479	1,1043
39,80	3,1302	1,2047

S: $C_A=0.0498$ M, $C_H=0.0997$ M, $C_{Na}=1.00$ M S: $C_A=0.0249$ M, $C_H=0.0498$ M, $C_{Na}=1.00$ M
T: $C_A=0.0504$ M, $C_H=0.0006$ M, $C_{Na}=1.00$ M T: $C_A=0.0259$ M, $C_H=0.0003$ M, $C_{Na}=1.00$ M
 $V_o=25.00$ ml $V_o=25.00$ ml

V_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	2,0948	1,8394
1,41	2,2616	1,7788
2,98	2,4106	1,7103
4,97	2,5775	1,6118
7,46	2,7428	1,5068
9,96	2,8784	1,4076
12,93	3,0110	1,3028
17,90	3,1853	1,1578
24,87	3,3716	1,0009
29,85	3,4774	0,9126

V_{tot}/ml	$-\log([H]/M)$	$\bar{n}_H$
0	2,2601	1,7809
1,41	2,3808	1,7226
2,98	2,4955	1,6609
4,97	2,6311	1,5776
7,46	2,7801	1,4773
9,95	2,9023	1,3849
12,93	3,0244	1,2854
16,91	3,1645	1,1719
22,88	3,3299	1,0330
29,85	3,4774	0,9071

Table 6. The over-all formation constants $\delta_{\underline{1}}^{25}$ for the proton diglycolate system with their estimated errors at 5, 20, 35, 50, and 65 °C.

$\underline{t}/^{\circ}\text{C}$	$\delta_1 \cdot 10^{-5}/\text{M}^{-1}$	$\delta_2 \cdot 10^{-6}/\text{M}^{-2}$
5.00	5.57±0.05	3.61±0.04
20.00	5.65±0.05	3.76±0.04
35.00	6.05±0.05	3.90±0.04
50.00	6.72±0.05	4.35±0.04
65.00	7.80±0.05	5.47±0.04

Table 7. The stepwise free energy changes $\underline{\Delta G}_1^{\circ}$ of the protonation of diglycolate at 5, 20, 35, 50, and 65 °C.

$\underline{t}/^{\circ}\text{C}$	$\frac{-\underline{\Delta G}_1^{\circ}}{\text{kcal}\cdot\text{mol}^{-1}}$	$\frac{-\underline{\Delta G}_2^{\circ}}{\text{kcal}\cdot\text{mol}^{-1}}$
5.00	4.75±0.01	3.60±0.01
20.00	5.03±0.01	3.78±0.01
35.00	5.33±0.01	3.96±0.01
50.00	5.66±0.01	4.15±0.01
65.00	6.02±0.01	4.40±0.01

Table 8. Corresponding values of v , $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the praseodymium diglycolate system at 5.00 °C. $V_0(S)=25.00$ ml.

S: $C_M=0.01990$ M, $C_H=0.00038$ M, $C_{Na}=1.00$ M T: $C_M=0.01990$ M, $C_H=0.00038$ M, $C_{Na}=1.00$ M
 $C_M=0.01990$ M, $C_A=0.20000$ M. $C_M=0.01990$ M, $C_A=0.20000$ M,
 $C_H=0.13736$ M, $C_{Na}=1.00$ M $C_H=0.19998$ M, $C_{Na}=1.00$ M

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$	v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1.00	2.2822	0.3730	5.6760	1.00	2.1427	0.3619	5.5683
1.49	2.1717	0.5259	5.4082	1.49	2.0304	0.5021	5.4624
1.74	2.1391	0.5869	5.3392	1.99	1.9743	0.6188	5.2809
1.99	2.1101	0.6639	5.2291	3.23	1.9303	0.8106	4.9594
2.49	2.0866	0.7817	5.0500	4.97	1.9542	1.0734	4.8277
3.23	2.0866	0.9254	4.8258	7.46	2.0314	1.3077	4.6310
3.98	2.1101	1.0610	4.6135	11.44	2.1510	1.5987	3.9513
4.97	2.1554	1.2258	4.3891	13.43	2.2097	1.7169	3.6910
5.97	2.2043	1.3564	4.1811	15.92	2.2713	1.8351	3.5067
6.97	2.2550	1.4851	4.0058	21.39	2.3836	2.0344	3.2151
7.97	2.3076	1.6017	3.8438	24.87	2.4380	2.1273	3.0774
9.45	2.3872	1.7537	3.6225	29.85	2.4959	2.2340	2.9511
10.00	2.4108	1.8079	3.5567				
11.00	2.4579	1.8905	3.4357				
12.50	2.5267	2.0053	3.2650				
14.00	2.5865	2.1061	3.1206				
16.00	2.6571	2.2192	2.9552				
18.50	2.7278	2.3364	2.7914				
21.50	2.7984	2.4450	2.6319				
25.00	2.8636	2.5403	2.4876				
30.00	2.9379	2.6287	2.3269				

S: $C_M=0.01990$ M, $C_A=0.20000$ M, $C_H=0.19960$ M, $C_{Na}=1.00$ M

T: $C_M=0.01990$ M, $C_H=0.00038$ M, $C_{Na}=1.00$ M

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
6.00	2.7459	2.6518	2.3122
10.00	2.6698	2.5466	2.4978
15.00	2.5865	2.3983	2.7066
17.00	2.5557	2.3402	2.7820
22.00	2.4814	2.2054	2.9681

Table 9. Corresponding values of v , $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the praseodymium diglycolate system at 20.00 °C. $V_o(s) = 25.00$ ml.

B: $C_M = 0,01990$, $C_H = 0,00038$, $C_{Na} = 1,00$ S: $C_M = 0,01990$, $C_H = 0,0038$, $C_{Na} = 1,00$

T: $C_M = 0,01990$, $C_A = 0,20000$, T: $C_M = 0,01990$, $C_A = 0,20000$

$C_H = 0,13736$, $C_{Na} = 1,00$

$C_H = 0,19998$, $C_{Na} = 1,00$

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,25	2,2289	0,4488	5,4459
1,49	2,1808	0,5219	5,3688
1,74	2,1499	0,5906	5,2598
1,99	2,1292	0,6544	5,1620
2,49	2,1069	0,7709	4,9963
3,23	2,1086	0,9192	4,7742
3,98	2,1344	1,0487	4,5695
4,97	2,1791	1,2130	4,3523
5,97	2,2341	1,3404	4,1344
6,97	2,2839	1,4693	3,9637
7,97	2,3355	1,5860	3,8058
9,45	2,4111	1,7391	3,5942
10,95	2,4850	1,8722	3,4024
12,44	2,5485	1,9888	3,2432
13,93	2,6121	2,0845	3,0927
15,92	2,6792	2,1978	2,9344
18,40	2,7496	2,3121	2,7726
21,39	2,8184	2,4194	2,6173
24,87	2,8785	2,5191	2,4820
29,85	2,9524	2,6050	2,3228
34,82	3,0040	2,6690	2,2109
39,80	3,0435	2,7146	2,1256

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,49	2,0502	0,4906	5,3712
1,99	1,9900	0,6083	5,2339
3,23	1,9488	0,8269	4,9247
4,97	1,9780	1,0458	4,5862
7,46	2,0553	1,2859	4,2251
11,44	2,1756	1,5796	3,8179
13,43	2,2306	1,6945	3,6570
15,92	2,2908	1,8167	3,4891
21,39	2,3990	2,0161	3,2043
24,87	2,4523	2,1081	3,0692
29,85	2,5073	2,2160	2,9284

Table 10. Corresponding values of v , $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the praseodymium diglycolate system at 35.00 °C. $V_o(\underline{s})=25.00$ ml.

S: $C_M=0.01990$ M, $C_H=0.00038$ M, $C_{Na}=1.00$ M S: $C_M=0.01990$ M, $C_H=0.00038$ M, $C_{Na}=1.00$ M
T: $C_M=0.01990$ M, $C_A=0.20000$ M, T: $C_M=0.01990$ M, $C_A=0.20000$ M,
 $C_H=0.13736$ M, $C_{Na}=1.00$ M $C_H=0.19998$ M, $C_{Na}=1.00$ M

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,00	2,2907	0,3701	5,6121
1,25	2,2269	0,4495	5,4784
1,49	2,1828	0,5209	5,3736
1,74	2,1517	0,5896	5,2679
1,99	2,1288	0,6544	5,1809
2,49	2,1060	0,7711	5,0162
3,23	2,1076	0,9193	4,7943
3,98	2,1370	1,0466	4,5803
4,97	2,1861	1,2083	4,3537
5,97	2,2368	1,3374	4,1458
6,97	2,2891	1,4645	3,9706
7,97	2,3430	1,5793	3,8083
9,45	2,4199	1,7306	3,5952
10,95	2,4935	1,8626	3,4049
12,44	2,5556	1,9789	3,2487
13,93	2,6194	2,0732	3,0986
15,92	2,6848	2,1865	2,9435
18,40	2,7551	2,2998	2,7828
21,39	2,8254	2,4043	2,6262
24,87	2,8842	2,5052	2,4938
29,85	2,9578	2,5921	2,3357
34,82	3,0101	2,6547	2,2233
39,80	3,0510	2,6971	2,1362

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,49	2,0389	0,4970	5,4490
1,99	1,9882	0,6092	5,2579
3,23	1,9490	0,8262	4,9401
4,97	1,9801	1,0431	4,5981
7,46	2,0569	1,2827	4,2387
11,44	2,1828	1,5702	3,8207
13,43	2,2368	1,6852	3,6635
15,92	2,2973	1,0849	3,4942
21,39	2,4035	2,0029	3,2141
24,87	2,4559	2,0941	3,0809
29,85	2,5131	2,1967	2,9367

Table 1. Corresponding values of $\log([H]/M)$, $\bar{n}$ and $-\log([A]/M)$ for various concentrations of baseodium diglycolate at 50.00 °C. $V_{\text{tot}}(ml) = 25.00$ ml.

$C_M = 0.01990$ M, $C_H = 0.00038$ M, $C_{Na} = 1.00$ M

$C_M = 0.01990$ M, $C_A = 0.20000$ M,

$C_H = 0.13736$ M, $C_{Na} = 1.00$ M

$C_M = 0.01990$ M, $C_H = 0.00038$ M, $C_{Na} = 1.00$ M

$C_M = 0.01990$ M, $C_A = 0.20000$ M,

$C_H = 0.13736$ M, $C_{Na} = 1.00$ M

v_{tot}/ml	$\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,00	2,2950	0,3686	5,6151
1,25	2,2342	0,4467	5,4718
1,49	2,1890	0,5183	5,3843
1,74	2,1593	0,5862	5,2788
1,99	2,1406	0,6488	5,1792
2,49	2,1219	0,7630	5,0100
3,23	2,1282	0,9085	4,7838
3,98	2,1578	1,0359	4,5758
4,97	2,2139	1,1945	4,3378
5,97	2,2654	1,3233	4,1320
6,97	2,3230	1,4476	3,9477
7,97	2,3761	1,5625	3,7894
9,45	2,4524	1,7132	3,5795
10,95	2,5242	1,8450	3,3944
12,44	2,5943	1,9537	3,2249
13,93	2,6489	2,0534	3,0924
15,92	2,7222	2,1569	2,9248
18,40	2,7908	2,2681	2,7683
21,39	2,8625	2,3666	2,6106
24,87	2,9249	2,4573	2,4738
29,85	2,9919	2,5510	2,3281
34,82	3,0480	2,6017	2,2108
39,80	3,0870	2,6454	2,1274

v_{tot}/ml	$\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,00	2,1531	0,3571	5,6515
1,49	2,0471	0,4923	5,4518
1,99	1,9988	0,6050	5,2710
3,23	1,9660	0,8141	4,9401
4,97	2,0003	1,0286	4,5574
7,46	2,0846	1,2635	4,2267
11,44	2,2077	1,5527	3,8182
13,43	2,2654	1,6633	3,6532
15,92	2,3277	1,7804	3,4827
21,39	2,4353	1,9721	3,2514
24,87	2,4852	2,0632	3,0739

Table 12. Corresponding values of v , $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the samarium diglycolate system at 5.00 °C. $V_o(s)=25.00$ ml.

: $C_M=0.01989$ M, $C_H=0.00058$ M, $C_{Na}=1.00$ M S: $C_M=0.01989$ M, $C_H=0.00058$ M, $C_{Na}=1.00$ M
: $C_M=0.01989$ M, $C_A=0.20000$ M, T: $C_M=0.01989$ M, $C_A=0.20000$,
 $C_H=0.13808$ M, $C_{Na}=1.00$ M $C_H=0.20058$ M, $C_{Na}=1.00$ M

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,49	2,1391	0,5373	5,6122
1,74	2,0993	0,6122	5,5120
1,99	2,0685	0,6831	5,4273
2,49	2,0268	0,8138	5,2836
3,23	2,0051	0,9787	5,0755
3,98	2,0087	1,1222	4,8911
4,97	2,0305	1,2892	4,6855
5,97	2,0667	1,4370	4,4962
6,97	2,1119	1,5687	4,3183
7,97	2,1554	1,6916	4,1651
9,45	2,2315	1,8496	3,9385
10,95	2,3039	1,9928	3,7392
12,44	2,3746	2,1169	3,5580
13,93	2,4398	2,2260	3,3973
15,92	2,5158	2,3533	3,2156
18,40	2,5955	2,4858	3,0301
21,39	2,6843	2,6024	2,8334
24,87	2,7730	2,6938	2,6436
29,85	2,8709	2,7749	2,4399

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,00	2,1174	0,3696	5,8684
1,49	1,9942	0,5206	5,6778
1,99	1,9254	0,6501	5,4996
4,97	1,8565	1,1448	4,8724
7,46	1,9073	1,4044	4,5368
11,44	2,0141	1,7105	4,1336
15,92	2,1355	1,9566	3,7789
21,39	2,2514	2,1759	3,4702
24,87	2,3130	2,2779	3,3155
29,85	2,3800	2,3964	3,1485
34,82	2,4325	2,4862	3,0198

Table 13. Corresponding values of $\underline{v}$, $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the samarium diglycolate system at 20.00 °C. $\underline{V}_o(s) = 25.00$ ml.

S: $C_M = 0.01989$ M, $C_H = 0.00058$ M, $C_{Na} = 1.00$ M S: $C_M = 0.01989$ M, $C_H = 0.00058$ M, $C_{Na} = 1.00$ M
T: $C_M = 0.01989$ M, $C_A = 0.20000$ M, T: $C_M = 0.01989$ M, $C_A = 0.20000$,
 $C_H = 0.13808$ M, $C_{Na} = 1.00$ M $C_H = 0.20058$ M, $C_{Na} = 1.00$ M

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$	v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,49	2,1413	0,5363	5,6106	1,00	2,1189	0,3688	5,8652
1,74	2,1017	0,6110	5,5132	1,49	1,9969	0,5188	5,6745
1,99	2,0725	0,6809	5,4223	1,99	1,9316	0,6455	5,4847
2,49	2,0364	0,8080	5,2587	3,23	1,8663	0,8906	5,1751
3,23	2,0158	0,9719	5,0569	4,97	1,8697	1,1328	4,8554
3,98	2,0227	1,1131	4,6881	7,46	1,9230	1,3905	4,5189
4,97	2,0485	1,2777	4,6574	11,44	2,0296	1,6971	4,1191
5,97	2,0880	1,4237	4,4638	15,92	2,1481	1,9447	3,7716
6,97	2,1310	1,5569	4,2938	21,39	2,2633	2,1629	3,4654
7,97	2,1791	1,6771	4,1321	24,87	2,3217	2,2670	3,3172
9,45	2,2530	1,8363	3,9122	29,85	2,3870	2,3858	3,1536
10,95	2,3251	1,9791	3,7151	34,82	2,4403	2,4734	3,0237
12,44	2,3922	2,1045	3,5419				
13,93	2,4557	2,2140	3,3857				
15,92	2,5279	2,3428	3,2116				
18,40	2,6121	2,4695	3,0187				
21,39	2,6923	2,5886	2,8309				
24,87	2,7788	2,6871	2,6528				

Table 14. Corresponding values of γ , $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the samarium diglycolate system at 35.00 °C. $V_o(\underline{s})=25.00$ ml.

S: $C_M=0.01989$ M, $C_H=0.00058$ M, $C_{Na}=1.00$ M S: $C_M=0.01989$ M, $C_H=0.00058$ M, $C_{Na}=1.00$ M
T: $C_M=0.01989$ M, $C_A=0.20000$ M, T: $C_M=0.01989$ M, $C_A=0.20000$ M,
 $C_H=0.13808$ M, $C_{Na}=1.00$ M $C_H=0.20058$ M, $C_{Na}=1.00$ M

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,00	2,2661	0,3989	5,7855
1,25	2,1942	0,4589	5,7031
1,49	2,1435	0,5352	5,6094
1,74	2,1059	0,6087	5,5020
1,99	2,0749	0,6795	5,4259
2,49	2,0438	0,8034	5,2439
3,23	2,0275	0,9647	5,0348
3,98	2,0389	1,1024	4,8392
4,97	2,0716	1,2626	4,6162
5,97	2,1092	1,4098	4,4314
6,97	2,1583	1,5394	4,2504
7,97	2,2073	1,6588	4,0895
9,45	2,2793	1,8184	3,8761
10,95	2,3545	1,9578	3,6749
12,44	2,4215	2,0812	3,5037
13,93	2,4836	2,1890	3,3513
15,92	2,5572	2,3131	3,1764
18,40	2,6341	2,4420	2,9983
21,39	2,7158	2,5593	2,8165
24,87	2,7959	2,6566	2,6440
29,85	2,8875	2,7441	2,4527
34,82	2,9562	2,7958	2,3116
39,80	3,0085	2,8396	2,2128

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,49	2,0046	0,5139	5,6339
1,99	1,9392	0,6321	5,4624
3,23	1,8819	0,8770	5,1407
4,97	1,8918	1,1127	4,8150
7,46	1,9474	1,3685	4,4803
11,44	2,0585	1,6708	4,0756
15,92	2,1730	1,9188	3,7392
21,39	2,2842	2,1354	3,4424
24,87	2,3430	2,2323	3,2885
29,85	2,4052	2,3534	3,1376

Table 14. Corresponding values of v , $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the samarium diglycolate system at 35.00 °C. $V_o(g) = 25.00$ ml.

S: $C_M = 0.01989$ M, $C_H = 0.00058$ M, $C_{Na} = 1.00$ M S: $C_M = 0.01989$ M, $C_H = 0.00058$ M, $C_{Na} = 1.00$ M
T: $C_M = 0.01989$ M, $C_A = 0.20000$ M, T: $C_M = 0.01989$ M, $C_A = 0.20000$,
 $C_H = 0.13808$ M, $C_{Na} = 1.00$ M $C_H = 0.20058$ M, $C_{Na} = 1.00$ M

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$	v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,00	2,2661	0,3989	5,7855	1,49	2,0046	0,5139	5,6339
1,25	2,1942	0,4589	5,7031	1,99	1,9392	0,6321	5,4624
1,49	2,1435	0,5352	5,6094	3,23	1,8819	0,8770	5,1407
1,74	2,1059	0,6087	5,5020	4,97	1,8918	1,1127	4,8150
1,99	2,0749	0,6795	5,4259	7,46	1,9474	1,3685	4,4803
2,49	2,0438	0,8034	5,2439	11,44	2,0585	1,6708	4,0756
3,23	2,0275	0,9647	5,0348	15,92	2,1730	1,9188	3,7392
3,98	2,0389	1,1024	4,8392	21,39	2,2842	2,1354	3,4424
4,97	2,0716	1,2626	4,6162	24,87	2,3430	2,2323	3,2885
5,97	2,1092	1,4098	4,4314	29,85	2,4052	2,3534	3,1376
6,97	2,1583	1,5394	4,2504				
7,97	2,2073	1,6588	4,0895				
9,45	2,2793	1,8184	3,8761				
10,95	2,3545	1,9578	3,6749				
12,44	2,4215	2,0812	3,5037				
13,93	2,4836	2,1890	3,3513				
15,92	2,5572	2,3131	3,1764				
18,40	2,6341	2,4420	2,9983				
21,39	2,7158	2,5593	2,8165				
24,87	2,7959	2,6566	2,6440				
29,85	2,8875	2,7441	2,4527				
34,82	2,9562	2,7958	2,3116				
39,80	3,0085	2,8396	2,2128				

Table 15. Corresponding values of v , $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the samarium diglycolate system at 50.00 $\% \frac{V_o(S)}{V_o(S)}$ = 25.00 ml.

S: $C_M=0.01989\text{ M}$, $C_H=0.00058\text{ M}$, $C_{Na}=1.00\text{ M}$

T: $C_M=0.01989\text{ M}$, $C_A=0.20000\text{ M}$,
 $C_H=0.13808\text{ M}$, $C_{Na}=1.00\text{ M}$

S: $C_M=0.01989\text{ M}$, $C_H=0.00058\text{ M}$, $C_{Na}=1.00\text{ M}$

T: $C_M=0.01989\text{ M}$, $C_A=0.20000$,
 $C_H=0.20058\text{ M}$, $C_{Na}=1.00\text{ M}$

v_{tot}/ml	$-\log([H]/\text{M})$	$\bar{n}$	$-\log([A]/\text{M})$	v_{tot}/ml	$-\log([H]/\text{M})$	$\bar{n}$	$-\log([A]/\text{M})$
1,00	2,2716	0,3775	5,7573	1,00	2,1266	0,3651	5,8336
1,25	2,2061	0,4541	5,6328	4,97	1,9161	1,0925	4,8005
1,49	2,1593	0,5280	5,5351	7,46	1,9785	1,3436	4,4474
1,74	2,1266	0,5985	5,4234	11,44	2,0907	1,6461	4,0562
1,99	2,1001	0,6662	5,3422	15,92	2,2108	1,8883	3,7113
2,49	2,0689	0,7892	5,1905	21,39	2,3230	2,0997	3,4151
3,23	2,0596	0,9451	4,9801				
3,98	2,0705	1,0836	4,7994				
4,97	2,1063	1,2424	4,5782				
5,97	2,1484	1,3875	4,3890				
6,97	2,1952	1,5189	4,2174				
7,97	2,2482	1,6364	4,0508				
9,45	2,3230	1,8013	3,8351				
10,95	2,3963	1,9335	3,6402				
12,44	2,4634	2,0552	3,4707				
13,93	2,5257	2,1610	3,3198				
15,92	2,6021	2,2796	3,1417				
18,40	2,6816	2,3973	2,9606				
21,39	2,7627	2,5125	2,7817				
24,87	2,8453	2,5993	2,6077				

Table 16. Corresponding values of $\underline{v}$, $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the dysprosium diglycolate system at 5.00 °C. $\underline{V}_o(\underline{s})=25.00$ ml.

S: $C_M=0.01994$ M, $C_H=0.00027$ M, $C_{Na}=1.00$ M S: $C_M=0.01994$ M, $C_H=0.00027$ M, $C_{Na}=1.00$ M
T: $C_M=0.01994$ M, $C_A=0.20000$ M, $C_M=0.01994$ M, $C_A=0.20000$ M,
 $C_H=0.13777$ M, $C_{Na}=1.00$ M $C_H=0.20027$ M, $C_{Na}=1.00$ M

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,25	2,2097	0,4449	5,6525
1,49	2,1590	0,5333	5,5371
1,74	2,1156	0,6086	5,4617
1,99	2,0848	0,6785	5,3761
2,49	2,0377	0,8104	5,2573
3,23	2,0014	0,9830	5,1000
3,98	1,9870	1,1373	4,9627
4,97	1,9996	1,3089	4,7703
5,97	2,0014	1,4777	4,6576
6,97	2,0232	1,6221	4,5242
7,97	2,0522	1,7520	4,3943
9,45	2,1083	1,9194	4,1987
10,95	2,1663	2,0709	4,0199
12,44	2,2260	2,2037	3,8528
13,93	2,2822	2,3235	3,7033
15,92	2,3619	2,4580	3,5068
18,40	2,4561	2,5942	3,2865
21,39	2,5648	2,7132	3,0463

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,00	2,1373	0,3666	5,7822
1,49	2,0159	0,5126	5,5768
1,99	1,9453	0,6403	5,4246
3,23	1,8620	0,8973	5,1806
4,97	1,8294	1,1708	4,9485
7,46	1,8457	1,4593	4,6827
11,44	1,9145	1,7915	4,3465
13,43	1,9544	1,9230	4,2052
15,92	2,0141	2,0540	4,0259
21,39	2,1119	2,2966	3,7449
24,87	2,1717	2,4097	3,5896
29,85	2,2478	2,5339	3,4005

Table 17. Corresponding values of v , $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the dysprosium diglycolate system at 20.00 °C. $V_o(\underline{s})=25.00$ ml.

S: $C_M=0.01994$ M, $C_H=0.00027$ M, $C_{Na}=1.00$ M S: $C_M=0.01994$ M, $C_H=0.00027$ M, $C_{Na}=1.00$ M
T: $C_M=0.01994$ M, $C_A=0.20000$ M, $C_M=0.01994$ M, $C_A=0.20000$ M,
 $C_H=0.13777$ M, $C_{Na}=1.00$ M $C_H=0.20027$ M, $C_{Na}=1.00$ M

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,25	2,2152	0,4562	5,6132
1,49	2,1619	0,5320	5,5321
1,74	2,1224	0,6053	5,4353
1,99	2,0897	0,6758	5,3670
2,49	2,0485	0,8041	5,2284
3,23	2,0124	0,9759	5,0792
3,98	2,0003	1,1283	4,9401
4,97	2,0003	1,3082	4,7862
5,97	2,0175	1,4665	4,6353
6,97	2,0485	1,6050	4,4824
7,97	2,0794	1,7338	4,3508
9,45	2,1378	1,9002	4,1531
10,95	2,1997	2,0491	3,9685
12,44	2,2598	2,1812	3,8024
13,93	2,3183	2,2987	3,6503
15,92	2,3939	2,4339	3,4633
18,40	2,4850	2,5696	3,2509
21,39	2,5915	2,6861	3,0165

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,49	2,0244	0,5074	5,5379
1,99	1,9522	0,6354	5,4092
3,23	1,8697	0,8907	5,1726
4,97	1,8543	1,1475	4,8993
7,46	1,8680	1,4380	4,6476
11,44	1,9402	1,7679	4,3091
13,43	1,9883	1,8922	4,1514
15,92	2,0416	2,0289	3,9872
21,39	2,1447	2,2650	3,6977
24,87	2,2031	2,3774	3,5459

Table 18. Corresponding values of v , $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the dysprosium diglycolate system at 35.00 °C. $V_{o(s)}=25.00$ ml.

S: $C_M=0.01994$ M, $C_H=0.00027$ M, $C_{Na}=1.00$ M S: $C_M=0.01994$ M, $C_H=0.00027$ M, $C_{Na}=1.00$ M
T: $C_M=0.01994$ M, $C_A=0.20000$ M, $C_M=0.01994$ M, $C_A=0.20000$ M,
 $C_H=0.13777$ M, $C_{Na}=1.00$ M $C_H=0.20027$ M, $C_{Na}=1.00$ M

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,00	2,2858	0,3740	5,7660
1,25	2,2122	0,4573	5,6600
1,49	2,1599	0,5328	5,5654
1,74	2,1207	0,6060	5,4633
1,99	2,0896	0,6758	5,3849
2,49	2,0504	0,8028	5,2372
3,23	2,0209	0,9703	5,0673
3,98	2,1028	1,1197	4,9201
4,97	2,0226	1,2927	4,7440
5,97	2,0438	1,4483	4,5877
6,97	2,0765	1,5858	4,4345
7,97	2,1141	1,7103	4,2906
9,45	2,1779	1,8731	4,0851
10,95	2,2417	2,0202	3,8996
13,93	2,3659	2,2625	3,5748
15,92	2,4411	2,3942	3,3916
18,40	2,5294	2,5258	3,1868
21,39	2,6292	2,6404	2,9674

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,00	2,1370	0,3666	5,8213
1,49	2,0160	0,5124	5,6106
1,99	1,9490	0,5375	5,4413
3,23	1,8738	0,8868	5,1757
4,97	1,8574	1,1443	4,9083
7,46	1,8852	1,4209	4,6240
11,44	1,9735	1,7364	4,2544
13,43	2,0209	1,8610	4,1001
15,92	2,0782	1,9932	3,9296
21,39	2,1861	2,2207	3,6330
24,87	2,2466	2,3269	3,4785
29,85	2,3218	2,4416	3,2942

Table 19. Corresponding values of v , $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the dysprosium diglycolate system at 50.00 °C. $V_o(s)=25.00$ ml.

S: $C_M=0.01994$ M, $C_H=0.00027$ M, $C_{Na}=1.00$ M S: $C_M=0.01994$ M, $C_H=0.00027$ M, $C_{Na}=1.00$ M
T: $C_M=0.01994$ M, $C_A=0.20000$ M, $C_M=0.01994$ M, $C_A=0.20000$ M,
 $C_H=0.13777$ M, $C_{Na}=1.00$ M $C_H=0.20027$ M, $C_{Na}=1.00$ M

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,00	2,2841	0,3746	5,8380
1,25	2,2155	0,4561	5,6743
1,49	2,1625	0,5317	5,5918
1,74	2,1282	0,6024	5,4642
1,99	2,0970	0,6720	5,3929
2,49	2,0596	0,7946	5,2466
3,23	2,0315	0,9638	5,0792
3,98	2,0284	1,1099	4,9219
4,97	2,0424	1,2803	4,7401
5,97	2,0705	1,4318	4,5711
6,97	2,1079	1,5667	4,4104
7,97	2,1469	1,6908	4,2661
9,45	2,2186	1,8494	4,0473
10,95	2,2872	1,9933	3,8548
12,44	2,3573	2,1167	3,6739
13,93	2,4197	2,2275	3,5102
15,92	2,4945	2,3563	3,3381
18,40	2,5850	2,4808	3,1320
21,39	2,6816	2,5912	2,9212
24,87	2,7721	2,6841	2,7293

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,00	2,1469	0,3621	5,7568
1,49	2,0299	0,5041	5,5675
1,99	1,9660	0,6257	5,4095
3,23	1,8943	0,8698	5,1565
4,97	1,8818	1,1226	4,8911
7,46	1,9177	1,3927	4,5961
11,44	2,0034	1,7117	4,2382
13,43	2,0549	1,8332	4,0769
15,92	2,1141	1,9637	3,9041
21,39	2,2342	2,1773	3,5859
24,87	2,2919	2,2832	3,4383
29,85	2,3651	2,3949	3,2590

Table 20. Corresponding values of $\bar{v}$, $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the ytterbium diglycolate system at 5.00 °C. $V_o(\underline{s})=25.00$ ml.

S: $C_M=0.01978$ M, $C_H=0.00049$ M, $C_{Na}=1.00$ M S: $C_M=0.01978$ M, $C_H=0.00049$ M, $C_{Na}=1.00$ M
T: $C_M=0.01978$ M, $C_A=0.20000$ M, T: $C_M=0.01978$ M, $C_A=0.20000$ M,
 $C_H=0.13747$ M, $C_{Na}=1.00$ M $C_H=0.20009$ M, $C_{Na}=1.00$ M

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,49	2,1210	0,5496	5,8168
1,74	2,0757	0,6283	5,7104
1,99	2,0395	0,7033	5,6238
3,98	1,9453	1,1701	5,0855
4,97	1,9507	1,3484	4,8986
5,97	1,9743	1,5036	4,7212
6,97	2,0087	1,6396	4,5544
7,97	2,0540	1,7591	4,3864
9,45	2,1445	1,9060	4,1178
10,95	2,2423	2,0337	3,8604
12,44	2,3365	2,1440	3,6293
13,93	2,4144	2,2459	3,4427
15,92	2,5032	2,3644	3,2358
18,40	2,5937	2,4873	3,0299
21,39	2,6807	2,6048	2,8362
24,87	2,7676	2,6978	2,6494
29,85	2,8618	2,7851	2,4517
34,82	2,9324	2,8344	2,3059
39,80	2,9886	2,8567	2,1919

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,49	1,9797	0,5339	5,8190
4,97	1,7913	1,2117	5,0483
7,46	1,8185	1,4924	4,7457
11,44	1,9254	1,7913	4,3216
13,43	1,9942	1,8974	4,1197
15,92	2,0775	2,0094	3,8945
21,39	2,2297	2,1990	3,5108
24,87	2,2985	2,2950	3,3413
29,85	2,3746	2,4037	3,1570

Table 21. Corresponding values of v , $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the ytterbium diglycolate system at 20.00 °C. $V_o(\underline{s})=20.00$ ml.

S: $C_M=0.01918$ M, $C_H=0.00104$ M, $C_{Na}=1.00$ M S: $C_M=0.01918$ M, $C_H=0.00104$ M, $C_{Na}=1.00$ M
T: $C_M=0.01918$ M, $C_A=0.20000$ M, T: $C_M=0.01918$ M, $C_A=0.20000$ M,
 $C_H=0.16114$ M, $C_{Na}=1.00$ M $C_H=0.22114$ M, $C_{Na}=1.00$ M

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,50	1,9934	0,6708	5,6027
1,75	1,9591	0,7581	5,5142
2,00	1,9350	0,8385	5,4296
2,50	1,9075	0,9815	5,2743
3,25	1,8886	1,1699	5,1006
4,00	1,8921	1,3288	4,9420
5,00	1,9230	1,5033	4,7309
6,00	1,9677	1,6512	4,5343
7,00	2,0313	1,7719	4,3247
8,00	2,1017	1,8765	4,1218
9,50	2,2220	2,0025	3,8145
11,00	2,3269	2,1124	3,5607
12,50	2,4128	2,2093	3,3580
14,00	2,4815	2,2959	3,1979
16,00	2,5554	2,3940	3,0274
18,50	2,6293	2,4916	2,8588
21,50	2,6963	2,5844	2,7070
25,00	2,7616	2,6563	2,5636
30,00	2,8287	2,7277	2,4156
35,00	2,8802	2,7682	2,3041
40,00	2,9180	2,7981	2,2225

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
0,50	2,2066	0,2488	6,1949
1,00	1,9814	0,4667	5,9003
1,50	1,8749	0,6406	5,6607
3,25	1,7598	1,0669	5,2147
5,00	1,7598	1,3353	4,9322
7,50	1,8079	1,6036	4,6219
11,50	1,9556	1,8558	4,1461
16,50	2,1258	2,0577	3,6968
21,50	2,2444	2,1996	3,4018
25,00	2,3011	2,2787	3,2613
30,00	2,3647	2,3628	3,1062

Table 22. Corresponding values of $\bar{v}$, $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the ytterbium diglycolate system at 35.00 °C. $\bar{v}_0(s)=25.00$ ml.

S: $C_M=0.01978$ M, $C_H=0.00049$ M, $C_{Na}=1.00$ M S: $C_M=0.01978$ M, $C_H=0.00049$ M, $C_{Na}=1.00$ M
T: $C_M=0.01978$ M, $C_A=0.20000$ M, T: $C_M=0.01978$ M, $C_A=0.20000$ M,
 $C_H=0.13747$ M, $C_{Na}=1.00$ M $C_H=0.20009$ M, $C_{Na}=1.00$ M

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,25	2,1828	0,4690	5,9278
1,49	2,1272	0,5485	5,8102
1,74	2,0814	0,6274	5,7233
2,49	2,0013	0,8365	5,4563
3,23	1,9670	1,0418	5,2584
3,48	1,9521	1,1693	5,1067
4,97	1,9670	1,3414	4,8945
5,97	1,9948	1,4940	4,7100
6,97	2,0405	1,6242	4,5206
7,97	2,0994	1,7360	4,3246
9,45	2,2122	1,8711	4,0151
10,95	2,3398	1,9805	3,7048
12,44	2,4509	2,0755	3,4485
13,93	2,5392	2,1619	3,2484
15,92	2,6308	2,2641	3,0436
18,40	2,7207	2,3676	2,8459
21,39	2,8009	2,4690	2,6704
24,87	2,8728	2,5580	2,5158
29,85	2,9545	2,6368	2,3444

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,49	1,9801	0,5353	5,8710
3,23	1,8247	0,9355	5,3435
4,97	1,0818	1,2056	5,0590
7,46	1,8427	1,4733	4,7246
11,44	1,9670	1,7602	4,2695
15,92	2,1501	1,9529	3,7857
21,39	2,3267	2,1083	3,3615
24,87	2,3986	2,1890	3,1899
29,85	2,4787	2,2735	3,0015

Table 23. Corresponding values of v , $-\log[H]$, $\bar{n}$ and $-\log[A]$ for the ytterbium diglycolate system at 50.00 °C. $V_o(s)=25.00$ ml.

S: $C_M=0.01978$ M, $C_H=0.00049$ M, $C_{Na}=1.00$ M S: $C_M=0.01978$ M, $C_H=0.00049$ M, $C_{Na}=1.00$ M
 T: $C_M=0.01978$ M, $C_A=0.20000$ M, T: $C_M=0.01978$ M, $C_A=0.20000$ M,
 $C_H=0.13747$ M, $C_{Na}=1.00$ M $C_H=0.20009$ M, $C_{Na}=1.00$ M

v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$	v_{tot}/ml	$-\log([H]/M)$	$\bar{n}$	$-\log([A]/M)$
1,00	2,2591	0,3818	6,0847	1,99	1,9036	0,6729	5,7256
1,25	2,1843	0,4684	5,9512	11,44	1,9738	1,7549	4,3024
1,49	2,1282	0,5480	5,8527	13,43	2,0642	1,8446	4,0590
1,74	2,0845	0,6258	5,7425	15,92	2,1718	1,9359	3,7897
1,99	2,0502	0,6996	5,6507	21,39	2,3651	2,0720	3,3356
2,49	2,0034	0,8351	5,4920	24,87	2,4431	2,1410	3,1538
3,48	1,9645	1,0635	5,2364	29,85	2,5210	2,2211	2,9710
3,98	1,9629	1,1617	5,1191				
4,97	1,9722	1,3378	4,9270				
5,97	2,0065	1,4862	4,7280				
6,97	2,0502	1,6177	4,5438				
7,97	2,1126	1,7282	4,3427				
9,45	2,2342	1,8588	4,0168				
10,95	2,3683	1,9645	3,6961				
12,44	2,4914	2,0502	3,4186				
13,93	2,5959	2,1212	3,1915				
15,92	2,6910	2,2137	2,9834				
18,40	2,7799	2,3099	2,7905				
21,39	2,8609	2,4006	2,6169				
24,87	2,9311	2,4815	2,4671				
29,85	3,0075	2,5578	2,3068				
34,82	3,0605	2,6574	2,2008				

Table 2. Stability constants β_1^{25} for the complexes of samarium, dysprosium and ytterbium diglycolate systems with their corresponding standard deviations at 5, 20, 35, and 50 °C.

Stability constant	β_1/M^{-1}	β_2/M^{-2}	β_3/M^{-3}
Temperature			
Metal Ion ↓	5 °C		
Pr	$(2.66 \pm 0.09) 10^5$	$(2.53 \pm 0.09) 10^9$	$(9.84 \pm 0.36) 10^{11}$
Sm	$(4.17 \pm 0.21) 10^5$	$(1.15 \pm 0.06) 10^{10}$	$(1.24 \pm 0.06) 10^{13}$
Dy	$(2.67 \pm 0.12) 10^5$	$(1.44 \pm 0.06) 10^{10}$	$(4.70 \pm 0.21) 10^{13}$
Yb	$(5.85 \pm 0.27) 10^5$	$(3.77 \pm 0.15) 10^{10}$	$(4.02 \pm 0.21) 10^{13}$
Temperature			
Metal Ion ↓	20 °C		
Pr	$(2.25 \pm 0.09) 10^5$	$(1.88 \pm 0.09) 10^9$	$(6.54 \pm 0.33) 10^{11}$
Sm	$(4.19 \pm 0.18) 10^5$	$(1.02 \pm 0.03) 10^{10}$	$(1.07 \pm 0.06) 10^{13}$
Dy	$(2.61 \pm 0.12) 10^5$	$(1.23 \pm 0.03) 10^{10}$	$(3.25 \pm 0.15) 10^{13}$
Yb	$(5.03 \pm 0.30) 10^5$	$(3.48 \pm 0.15) 10^{10}$	$(2.53 \pm 0.15) 10^{13}$
Temperature			
Metal Ion ↓	35 °C		
Pr	$(2.41 \pm 0.09) 10^5$	$(1.98 \pm 0.09) 10^9$	$(6.69 \pm 0.30) 10^{11}$
Sm	$(4.03 \pm 0.15) 10^5$	$(8.33 \pm 0.39) 10^9$	$(7.46 \pm 0.42) 10^{12}$
Dy	$(3.13 \pm 0.12) 10^5$	$(1.20 \pm 0.03) 10^{10}$	$(2.29 \pm 0.12) 10^{13}$
Yb	$(6.52 \pm 0.33) 10^5$	$(3.70 \pm 0.18) 10^{10}$	$(1.53 \pm 0.09) 10^{13}$
Temperature			
Metal Ion ↓	50 °C		
Pr	$(2.39 \pm 0.12) 10^5$	$(1.82 \pm 0.09) 10^9$	$(5.12 \pm 0.33) 10^{11}$
Sm	$(3.35 \pm 0.18) 10^5$	$(6.12 \pm 0.33) 10^9$	$(4.27 \pm 0.30) 10^{12}$
Dy	$(3.12 \pm 0.18) 10^5$	$(1.11 \pm 0.06) 10^{10}$	$(1.55 \pm 0.12) 10^{13}$
Yb	$(6.78 \pm 0.36) 10^5$	$(4.11 \pm 0.21) 10^{10}$	$(1.15 \pm 0.09) 10^{13}$

Table 25. The stepwise free energy changes ΔG_i° of the complex formation of the praseodymium, samarium, dysprosium and ytterbium diglycolate systems at 5, 20, 35, and 50 °C.

	ΔG_1° kcal·mol ⁻¹	ΔG_2° kcal·mol ⁻¹	ΔG_3° kcal·mol ⁻¹
Temperature → Metal Ion ↓	5 °C		
Pr	6.90±0.02	5.06±0.04	3.29±0.04
Sm	7.15±0.03	5.54±0.04	3.35±0.06
Dy	6.90±0.03	6.02±0.05	4.47±0.05
Yb	7.33±0.02	6.11±0.04	3.85±0.05
Temperature → Metal Ion ↓	20 °C		
Pr	7.18±0.02	5.26±0.05	3.41±0.06
Sm	7.54±0.03	5.88±0.04	4.05±0.05
Dy	7.26±0.03	6.27±0.05	4.59±0.05
Yb	7.64±0.03	6.49±0.06	3.84±0.06
Temperature → Metal Ion ↓	35 °C		
Pr	7.59±0.02	5.52±0.05	3.57±0.05
Sm	7.90±0.02	6.09±0.05	4.16±0.06
Dy	7.75±0.02	6.46±0.04	4.63±0.05
Yb	8.18±0.03	6.72±0.06	3.69±0.06
Temperature → Metal Ion ↓	50 °C		
Pr	7.96±0.03	5.75±0.06	3.63±0.07
Sm	8.17±0.03	6.31±0.07	4.21±0.07
Dy	8.13±0.04	6.74±0.07	4.65±0.08
Yb	8.63±0.03	7.08±0.07	3.63±0.08

Table 26. The stepwise free energy functions $\frac{\Delta G_i^\circ}{T} = \frac{A}{T} + \frac{B}{T} + C \ln(T/K) + \frac{DT}{T} + \frac{ET^2}{T}$ for the samarium diglycolato complexes and for diglycolic acid.

	Constants →	$\frac{A}{\text{kcal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$	$\frac{-E}{\text{kcal}\cdot\text{mol}^{-1}}$	$\frac{-C}{\text{kcal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$	$\frac{D\cdot 10^3}{\text{kcal}\cdot\text{mol}^{-1}\cdot\text{K}^{-2}}$	$\frac{-E\cdot 10^6}{\text{kcal}\cdot\text{mol}^{-1}\cdot\text{K}^{-3}}$
Sm- diglyc.	$\frac{\Delta G_1^\circ}{T}$	5.952181	119.900	1.142185	3.759520	2.123457
	$\frac{\Delta G_2^\circ}{T}$	7.891845	159.179	1.505553	4.639253	2.617284
	$\frac{\Delta G_3^\circ}{T}$	9.254303	180.570	1.735634	5.821404	3.162494
Tiglyc. Acid	$\frac{\Delta G_1^\circ}{T}$	11.345559	221.569	2.178046	7.223716	4.024692
	$\frac{\Delta G_2^\circ}{T}$	15.671475	307.695	3.602663	9.867164	5.456790

Fig. 1. The plots of $\bar{n}$ versus $\log[A]$ for the praseodymium diglycolate system at 5, 20, 35, and 50 °C. The values of $\underline{a}$ are for the various temperatures beginning at 5 °C: -6.00, -6.50, -7.00, and -7.50.

Fig. 2. The stepwise free energy changes $\frac{\Delta G_1^{\circ}}{T}$ and $\frac{\Delta G_2^{\circ}}{T}$ for the formation of diglycolic acid as functions of temperature. The values ($\otimes$) at 25 °C are taken from the work of Grenthe and Hansson²². The full drawn curves in this Figure and Figures 3 and 4 are calculated according to the equations given in Table 26.

Fig. 3 and 4. The stepwise free energy changes $\frac{\Delta G_1^{\circ}}{T}$, $\frac{\Delta G_2^{\circ}}{T}$, and $\frac{\Delta G_3^{\circ}}{T}$ for the samarium diglycolate system as functions of temperature.

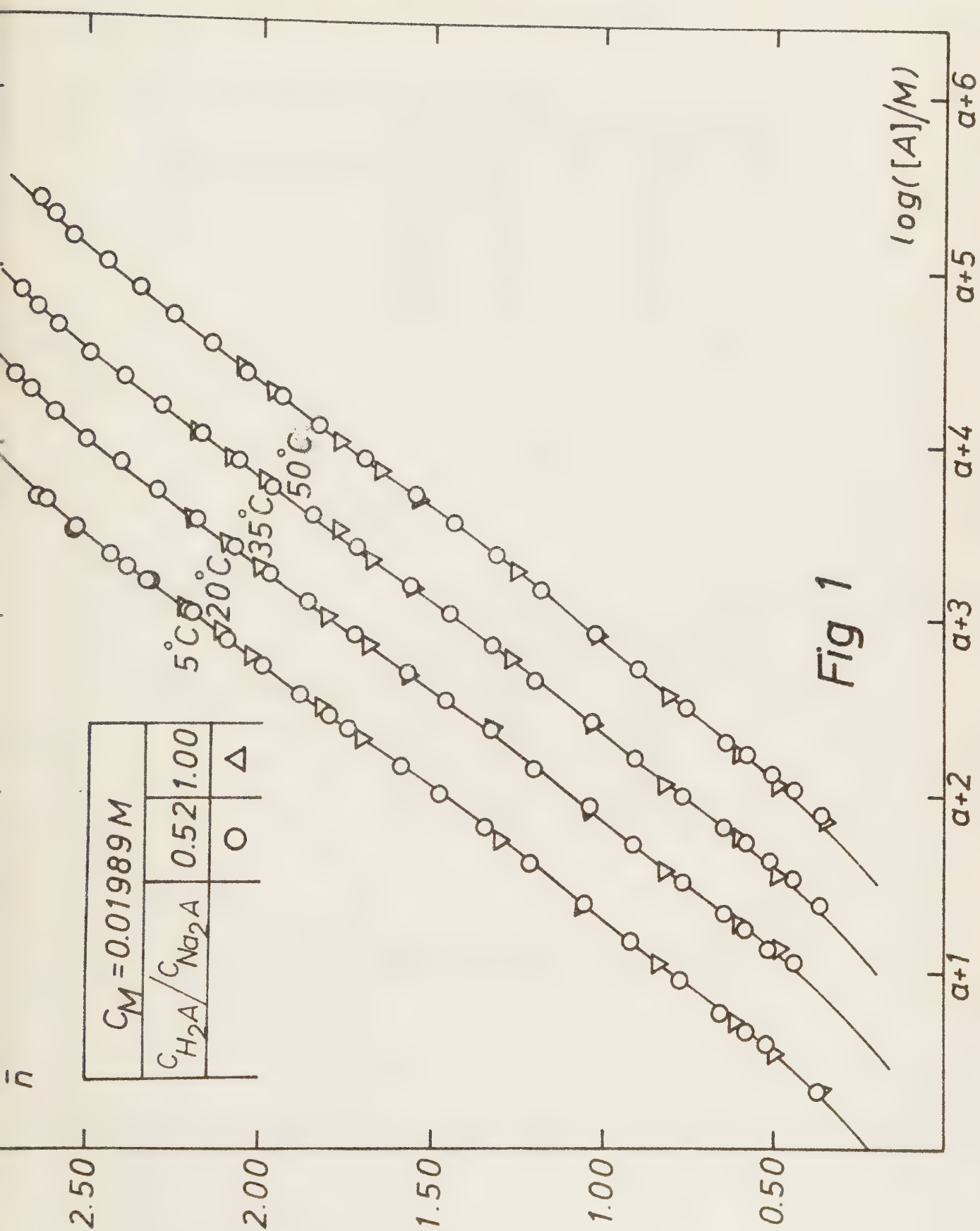


Fig 1

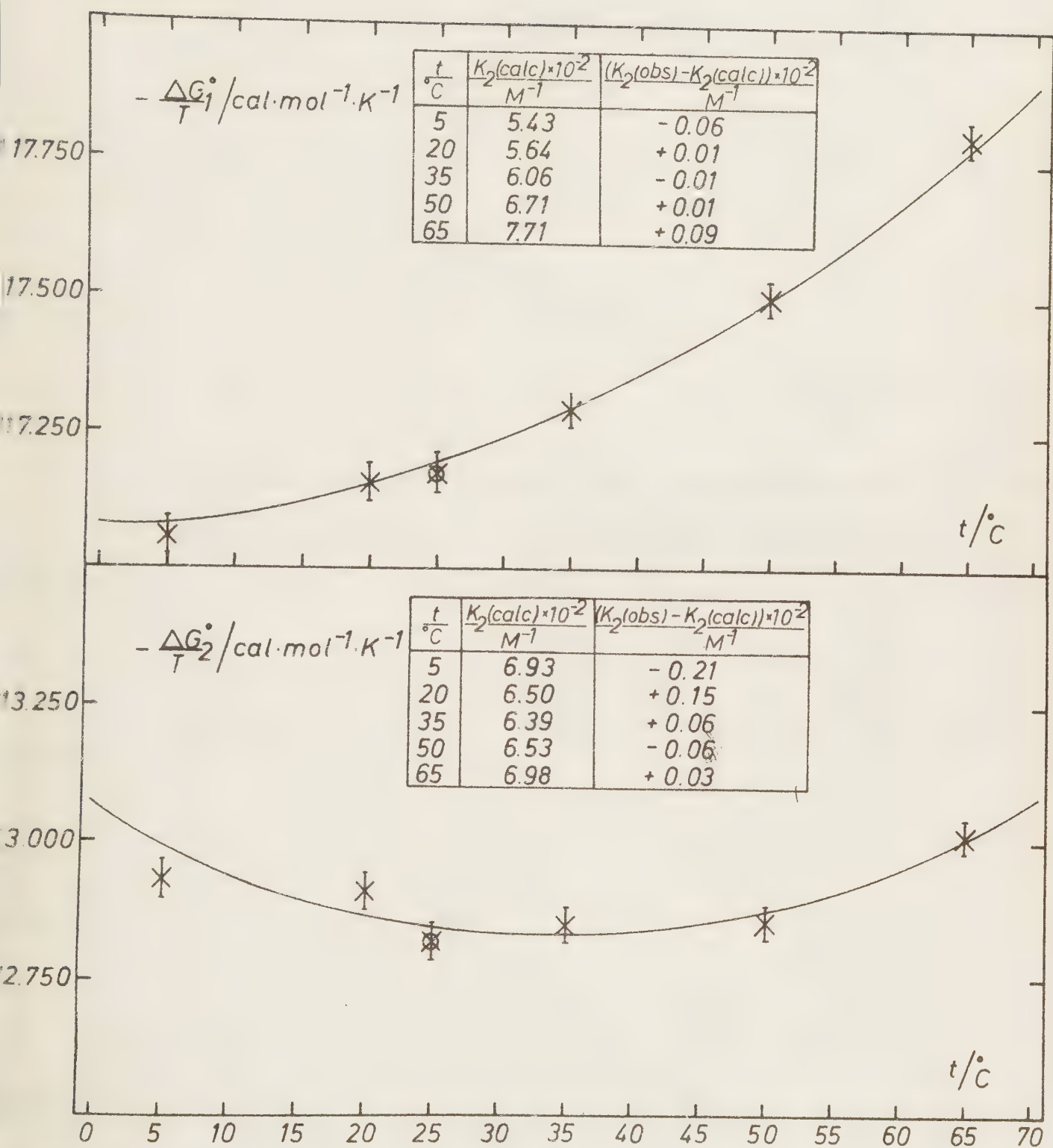
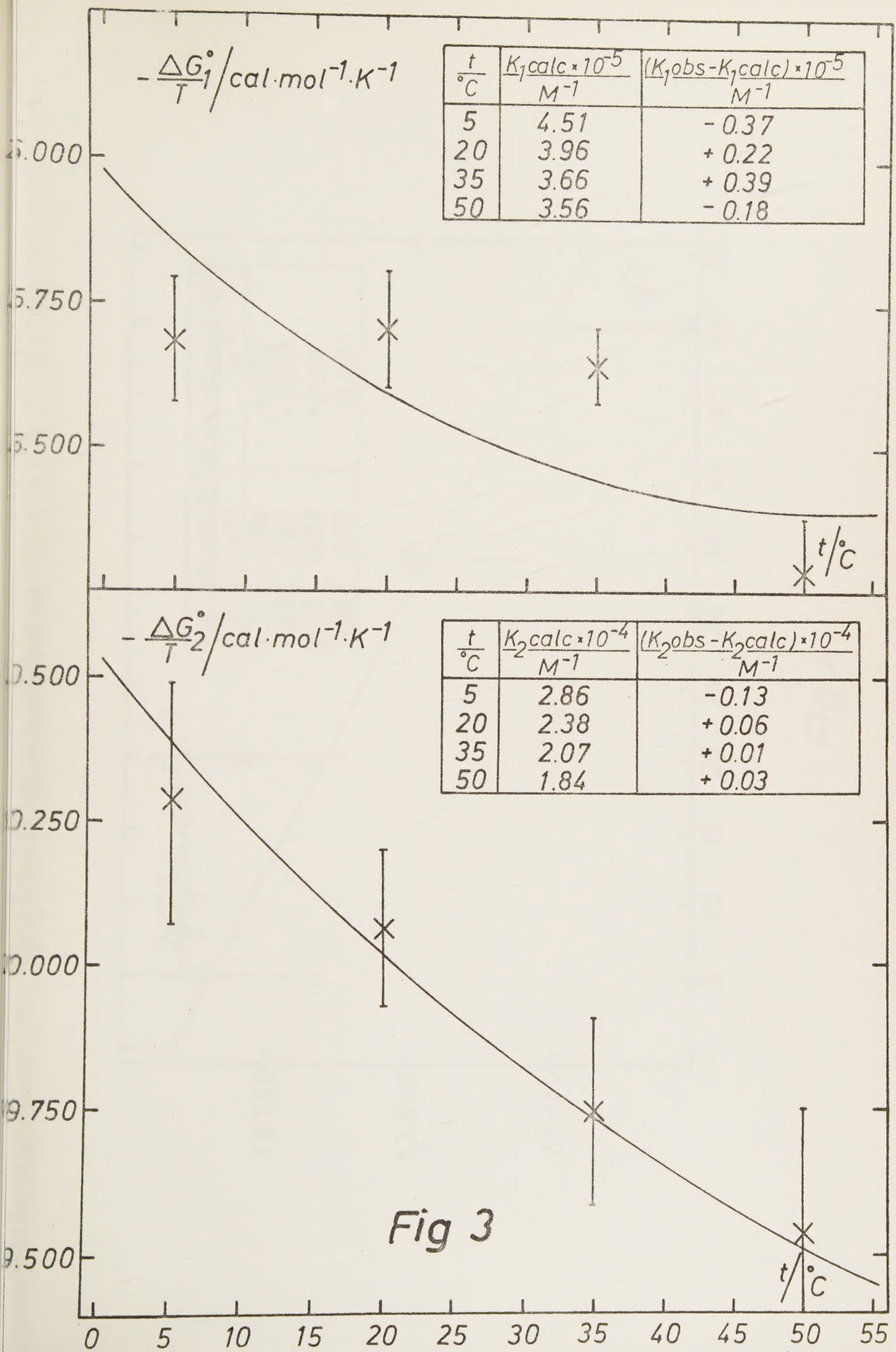


Fig 2



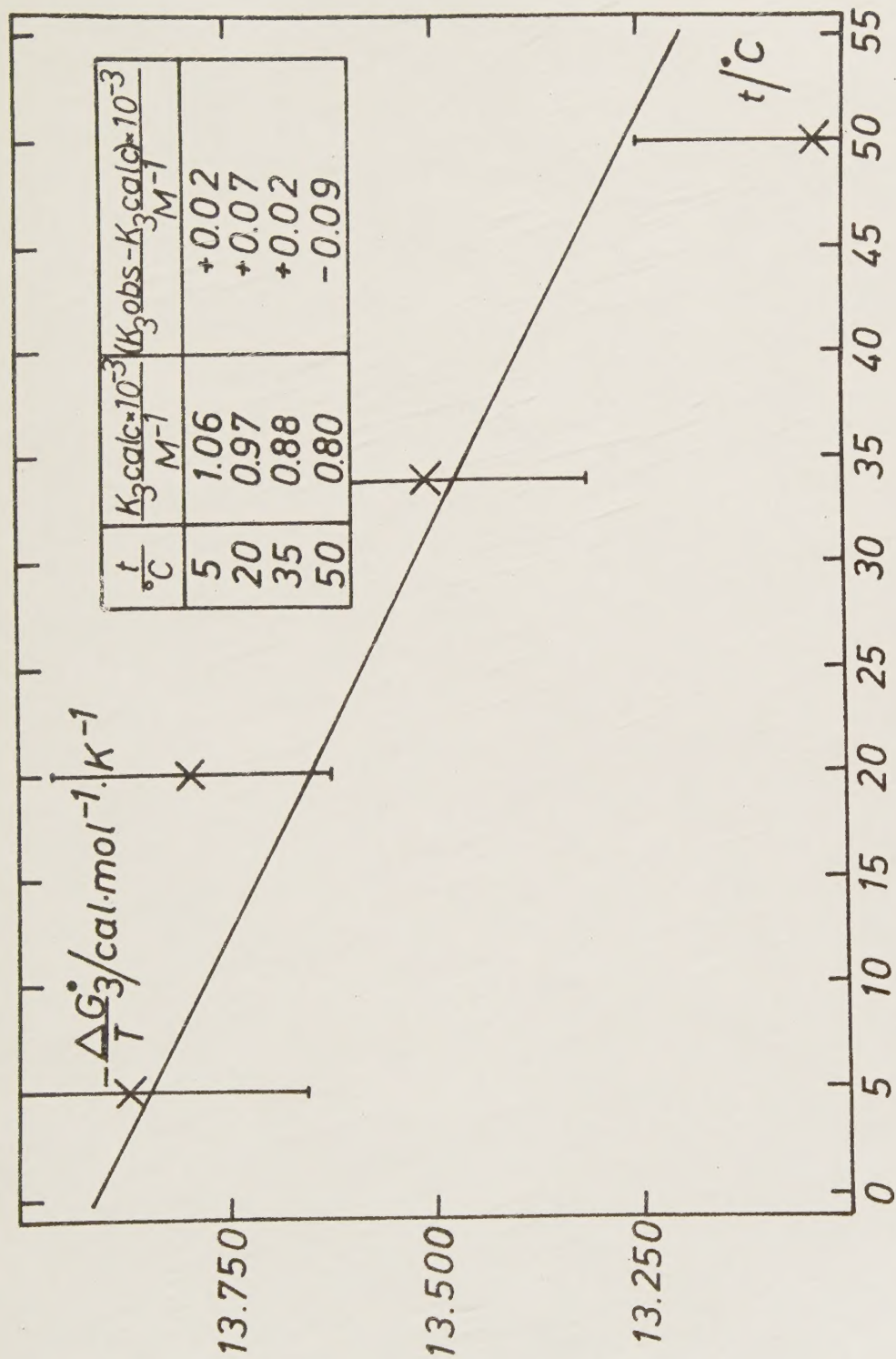


Fig 4

